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PARACHORS AND STRUCTURE OF DIALKYLPHOSPHOROUS ACIDS

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/Tables referred to are appended./

/This paper reports additional results obtained in the extensive investigation on organic phosphorus compounds being carried out at the University of Kazan. Dialkylphosphorous acid esters may serve as starting materials in the synthesis of nerve poisons. The physical properties studied in this instance affect the reactivity and volatility of these esters. Published articles contain no direct evidence that the group of Russian investigators in question is actually engaged in the synthesis of nerve poisons; however this is a distinct possibility./

Preceding reports (1) presented data on the parachors of the dialkylphosphorous acids from dimethyl- to dioctyl-phosphorous acid in the homologous series. The values calculated for the parachors and the values found were in close conformity with each other as far as dibutylphosphorous acid. At this point, a divergence between the computed and found values was observed, the deviation having a constant value from dihexyl- to dioctylphosphorous acid.

The deviation was explained at that time by the authors on the basis of the assumption that liquid dialkylphosphorous acids are dimers, an opinion supported by the results of a previous investigation (2) in which the spectra of these compounds were investigated by the combined light scattering method.

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Calculation of parachors for the dimer forms while introducing a correction for the parallelism of the four ester radical chains of the dimer form gave values which conformed closely to the found values.

However, the interaction assumed for the four ester radical chains of the dimer form cannot be explained from a purely geometric point of view because it is then necessary to assume that the ring formed by hydrogen bonding does not lie in a flat plane, a fact which is not probable.

Besides, as was later shown with esters of ortho acids (3, 4) and with tertiary amines (5), when there are three or four chains starting from a central atom, an interaction does not occur among all of the chains, and the molecule has a tendency to assume a stretched-out form.

Because previous studies have been incomplete, the authors were prompted in this work to delve further into the investigation of the parachors and structure of dialkylphosphorous acids.

They begin by observing that Gibling (6) established the effect of association on the size of the molecular parachor in the case of fatty acids. The standard difference in the value for the parachors encountered in passing from one member of the homologous series to the next (the additional group being CH_2 in each case) is equal to 39.8 units. The size of this difference ΔCH_2 depends on the magnitude of the parachor (correction for expansion). For parachors of 730 to 1,556 units, the difference increases from 40.5 to 41.1 units.

Through calculation of parachors for the aliphatic acids from experimental values, Gibling arrived at the conclusion that the higher aliphatic acids occur in the dimer state at the temperature at which their parachors are measured.

Calculations similar to Gibling's were made by the authors for dialkylphosphorous acids, under inclusion of corrections for interaction. The differences between the experimental values for the parachors of two consecutive members of the homologous series (the additional group again being CH_2 in each case) are listed in Table 1.

From Table 1 it is seen that the average value $\Delta CH_2 = 39.6$ is close to the standard value $\Delta CH_2 = 39.8$. For higher members of the series, beginning with dihexylphosphorous acid, $\Delta CH_2 = 40.2$, this value corresponding to parachors of the order of 400-700. If the higher members of the dialkylphosphorous acids were dimers with parachors of the order of 1200-1500, ΔCH_2 would be expected to equal 40.8-41.1 units, which is not the case. Therefore, it can be assumed that the higher members of the series are not associated.

To obtain supplementary data on the association of dialkylphosphorous acids, the authors measured the molecular weights of several of the acids by the cryoscopic method in a benzene solution. The measurements are given in Table 2.

The authors do not claim accuracy for the data on molecular weights for high concentrations, but they do feel that their figures permit the conclusion that dimethylphosphorous acid is associated and that it appears in the monomeric form only in very dilute solutions.

As shown in Table 2, the molecular weight of dioctylphosphorous acid corresponds closely to that for the monomeric form, and does not increase as the concentration increases, which fact makes it possible to state that the acid is monomeric in the liquid state.

Attempts to examine the spectra of dihexyl-, diheptyl- and dioctyl-phosphorous acids by the combined light scattering method were unsuccessful in view of their high boiling points and the consequent difficulty of obtaining them in an optically pure state.

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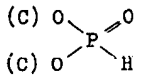
Proceeding then from the assumption that dioctylphosphorous acid is a monomer in the liquid state, the parachor of the group

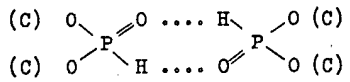


was computed from the experimental value for the parachor of the acid 764.0, introducing corrections for expansion, the deflection of the chains $2B = -2.8$, and the interactions of the chains among themselves $6(-2.2) = -13.2$. The group value was found to be 107.3.

Using this new group value, the authors calculated the parachors of the monomeric forms of the remainder of the dialkylphosphorous acids, presenting their results along with the found values for the parachors in Table 3.

This table indicates that only the three highest members of the series, judging by their parachors, are monomeric. Increasing deviations between the values computed and the values found for the parachors are shown for the lower members, signifying increased association of these members in the liquid state.

By assuming that dimethylphosphorous acid is a dimer in the liquid state, and consequently that the parachor of the group



is 229.8, then, by allowing for internal interactions of two pairs of chains among themselves pair by pair, the parachors of the dialkylphosphorous acids were calculated. These are given in Table 4.

Table 4 shows that only the first two lowest members are associated in the liquid state. Deviations in the values calculated for the parachors from those found indicate increased dissociation in the monomeric state for all of the latter members of the series.

The percentage of deviation, beginning with dihexylphosphorous acid and proceeding upward in the series, means that the last three dialkylphosphorous acids are monomeric in the liquid state.

If it is assumed that the percentage of deviation - 1.7 is characteristic of the monomeric state of the dialkylphosphorous acids, then the monomer percentages of the intermediate members of the series can be roughly calculated. It follows from this calculation that 65%, 70%, and 40% are the monomer percentages of diisobutyl-, dibutyl-, and di-propylphosphorous acids, respectively. These values are approximate and tentative only, because an error of 0.2% in the determination of the parachor results in a difference of 10% in the computed degree of association.

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[Tables follow.]

Table 1

Substance From	To	ΔCH_2	Used Value of Interaction Correction for Each ΔCH_2	ΔCH_2 Corrected
dimethyl-	diethyl-phosphorous acid	38.1	β 1.4	39.5
diethyl-	dipropyl-phosphorous acid	38.1	½ 1.1	39.2
dipropyl-	dibutyl-phosphorous acid	37.9	½ 1.1	39.0
dibutyl-	dihexylphos-phorous acid	38.2	½ 1.1	39.3
dihexyl-	diheptylphos-phorous acid	39.2	½ 1.1	40.3
diheptyl-	dioctyl-phosphorous acid	39.0	½ 1.1	40.1

Table 2

Conc in Mol Percent	Mol Wt.	ΔT
Dimethylphosphorous acid		
0.632	177.6	0.391
1.073	117.7	0.666
1.923	121.0	1.171
2.683	124.4	1.601
5.225	135.8	2.934
5.988	138.2	3.330
7.865	144.8	4.261
10.036	152.4	5.292
13.351	166.9	6.671
14.828	173.4	7.257
16.846	182.6	8.017
19.709	192.5	9.216
22.330	204.3	10.173
24.907	210.2	11.402
27.439	222.8	12.266

Conc in Mol Percent	Mol Wt	ΔT
Diisopropylphosphorous acid (figures from T. G. Shavsha)		
0.397	160.0	0.2740
2.733	170.3	1.8014
3.919	170.9	2.5760
4.967	174.9	3.2620
6.721	176.7	4.4503
9.288	180.9	6.1780
12.20	186.0	8.1633
16.37	191.3	11.1678
20.88	202.4	14.2345
Dioctylphosphorous acid		
0.951,	305.9	--
3.109	303.2	--
6.090	292.3	--
7.816	285.8	--
10.030	280.4	--
12.637	278.1	--

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Table 3

Dialkyl-phosphorous Acids	Standard Ideal Value	Correction For Expansion	Parachor Calculated	Parachor Found	Percent of Division	Corrections
Dioctyl	758.1	5.9	764.0	764.0	0	-16.0 2β6 II
Diheptyl	680.7	4.8	685.5	685.5	0	-13.8 2β5 II
Dihexyl	603.3	3.7	607.0	607.5	0	-11.6 2β4 II
Dibutyl	448.5	2.0	450.5	454.7	0.9	- 7.2 2β2 II
Diisobutyl	446.3	2.0	448.3	453.1	1.0	- 5.0 2β1 II
Dipropyl	371.1	1.3	372.4	378.9	1.8	- 5.0 2β1 II
Diisopropyl	365.3	1.3	366.6	377.8	3.0	- 5.6 4β
Diethyl	293.7	0.8	294.5	302.6	2.7	- 2.8 2β
Dimethyl	217.7	0.4	218.1	226.3	3.7	---- --

Table 4

Dialkyl-phosphorous Acids	Standard Ideal Value	Correction For Expansion	Parachor Calculated	Parachor Found	Percent of Division	Corrections
Dimethyl	450.6	2.05	454.65	452.65	0	- 5.6 4β
Diethyl	602.6	3.7	606.3	605.3	0.2	-10.0 4β2 II
Dipropyl	757.4	5.7	763.1	758.0	0.7	-11.2 8β
Diisopropyl	745.8	5.6	751.4	755.6	0.6	-14.4 4β4 II
Dibutyl	912.2	8.4	920.6	909.4	1.2	-10.0 4β2 II
Diisobutyl	907.8	8.2	916.0	906.2	1.1	-23.2 4β8 II
Dihexyl	1221.8	15.4	1237.2	1216.0	1.7	-27.6 4β10II
Diheptyl	1376.6	19.7	1396.3	1372.0	1.7	-32.0 4β12II
Dioctyl	1531.4	24.0	1555.4	1528.0	1.7	---- --

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